

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

\_\_\_\_\_ x

In re Application of: :  
     A. Nakajima et al. : Art unit: 1755  
 Serial No. 10/647,169 :  
 Filed: August 21, 2003 :  
 For: INK-JET IMAGE FORMING :  
     METHOD

\_\_\_\_\_ x

DECLARATION

Honorable Commissioner of Patents  
 and Trademarks  
 Washington, D.C. 20231

Sir:

I, Fumio ISHII hereby declare and say as follows:

I am familiar with both the English and Japanese languages and I have compared the annexed English translation with the Japanese text of Japanese Patent Application No. 252356/2002.

To the best of my knowledge and belief, the annexed English translation is an accurate translation of the above Japanese application.

The undersigned declares further that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like

so made are punishable by fine or imprisonment, or both under Section 1001 of Title 18 of the U.S. Code and that such willful false statements may jeopardize the validity of the above-identified application or any patent issuing thereon.

A handwritten signature in cursive script, appearing to read 'Fumio Ishii', written in dark ink.

---

Fumio ISHII

Dated: This 9th day of May, 2005.



**Patent Application No. 252356/2002**

**Title of the Document:** APPLICATION FOR PATENT

**Reference Number:** DKT2481557

**Address:** The Director General of the  
Patent Office

**International  
Patent Classification:** B41J 2/01  
B41M 5/00

**Inventor(s) ;**

**Post-Office Address:** C/O Konica Corporation  
1 Sakura-machi, Hino-shi,  
Tokyo, Japan

**Name:** Atsushi NAKAJIMA

**Applicant for patent:**

**Identification Number:** 000001270

**Name:** Konica Corporation

**Representative:** Fumio IWAI

**Indication of Fee:**

**Prepayment Registration  
Number:** 012265

**Amount of Payment** 21000

**List of Documents Attached:**

**Title of Document:** Specification 1

**Title of Document:** Abstract 1

**Necessity of Proof** Required



[NAME OF DOCUMENT] SPECIFICATION

[TITLE OF THE INVENTION]

INK-JET IMAGE FORMING METHOD

[WHAT IS CLAIMED IS:]

Claim 1. An oxetane compound having an electron-donating group and an electron-withdrawing group in the molecule, and further having a substituent at the 2-position of the molecule.

Claim 2. The oxetane compound of claim 1, wherein the electron-donating group is substituted at the 2-position of the molecule and the electron-withdrawing group is substituted at the 4-position of the molecule.

Claim 3. The oxetane compound of claim 1 or claim 2, having a substituent at the 3-position of the molecule.

Claim 4. The oxetane compound of any one of claims 1 to 3, wherein the oxetane compound has two or more oxetane groups in the molecule.

Claim 5. An ink-jet ink comprising a photo-acid generating compound and the oxetane compound of any one of claims 1 to 4.

Claim 6. The ink-jet ink of claim 5, wherein the oxetane compound has no substituent at the 2-position of the molecule.

Claim 7. The ink-jet ink of claim 5 or claim 6, further comprising an epoxy compound or a vinyl ether compound.

Claim 8. A method for forming an image, comprising the steps of:

jetting a droplet of the ink-jet ink of any one of claims 5 to 7 from an ink-jet head onto a recording material; and

irradiating the jetted droplet of the ink-jet ink with an active ray.

[DETAILED EXPLANATION OF THE INVENTION]

[0001]

[FIELD OF THE INVENTION]

The present invention relates to an oxetane compound, an ink-jet ink comprising the oxetane compound and an ink-jet image forming method using thereof. More specifically the present invention relates to a photo-curable ink-jet ink comprising an oxetane compound which is cationic polymerizable, and an ink-jet image forming method using the ink having high reactivity and producing high quality image.

[0002]

[PRIOR ART]

In recent years, an ink-jet recording method has found wide applications in the field of various kinds of graphic arts such as photography, various printing, marking and specific printing such as a color filter because of being able to form images simply and cheap. Particularly, it has come to be possible also to obtain image quality compatible with silver salt photography by utilizing a recording apparatus which ejects and controls fine dots; ink in which such as a color reproduction range, durability and ejection suitability have been improved; and exclusive paper in which such as ink absorption, color forming property of a colorant and surface gloss have been improved greatly. Image quality improvement of an ink-jet recording method of today has been achieved only when a complete set of a recording apparatus, ink and exclusive paper is prepared.

[0003]

However, an ink-jet system which requires exclusive paper is problematic in respect to limitation of a recording medium and cost up of a recording medium. Therefore, many attempts to record on a medium, on which ink is transferred, different from exclusive paper by means of an ink-jet recording. Concretely, there are such as a phase-conversion ink-jet method utilizing wax which is solid at room

temperature, a solvent-type ink-jet method utilizing an ink which is mainly comprised of a rapid-drying organic solvent and a UV ink-jet method in which an ink is cross-linked by ultraviolet (UV) light after recording.

[0004]

Among them, a UV ink-jet method has been noted recently in respect to relatively low odor compared to a solvent-type ink-jet method, rapid drying property and capability of recording on a recording medium without ink absorption property; UV-curable ink-jet ink is disclosed, for example, in Japanese Patent Publication No. 5-54667, JP-A (hereinafter, JP-A refers to Japanese Patent Publication Open to Public Inspection) No. 6-20204 and Japanese Translated PCT Patent Publication No. 2000-504778.

[0005]

It is known that the aforesaid UV ink can be divided mainly into a radical polymerization type and a cationic polymerization type. In an ultraviolet radiation curable ink-jet recording system, image quality, i.e. impinged dot diameter, is controlled by factors such as light exposure timing after ink impingement, illuminance of exposed light, energy, ink droplet size, photosensitivity of ink, surface

energy, viscosity, wettability of substrates, impingement pattern, and error diffusion pattern. Specifically, factors which mainly affect image quality are photosensitivity, viscosity, and surface tension of ink, wettability of substrates, and exposure conditions. Of these, when ink is cured by radical polymerization, photosensitivity is adversely affected by polymerization inhibition due to exposure to oxygen. As a result, the aforesaid photosensitivity largely depends on ink layer thickness and illuminance of exposing light. On the other hand, when ink is cured by cationic polymerization, photosensitivity is largely dependent on humidity, as well as temperature.

[0006]

When a radically polymerizable ultraviolet radiation curable ink is used, in order to minimize the polymerization inhibition due to exposure to oxygen, known are inventions in regard to monomers, initiators, and initiation aids which are free from oxygen inhibition, and methods in which purging is performed employing inert gases such as nitrogen.

[0007]

When a cationically polymerizable ultraviolet radiation curable ink is employed, in order to minimize the humidity



dependent effects, known is a method in which impinged ink is heated as disclosed in Japanese Patent Application Open to Public Inspection No. 2002-137375.

[0008]

Known as cationically polymerizable monomers employed in the cationically polymerizable ultraviolet radiation curable ink are epoxy compounds having oxirane ring(s), oxetane compounds, and vinyl ether compounds.

[0009]

In particular, it is known that by using epoxy compounds together with oxetane compounds, the polymerization rate increases markedly. For example, pertinent publications include Toa Gosei Kenkyu Nenpo (Toa Gosei Annual Research Report) TREND No. 2 (1999), "Oxetane Kagobutsu no Hikari Cation Koka System eno Oyo (Application of Oxetane Compounds to Cationically Photocurable System of Oxetane Compounds" and Japanese Patent Publication No. 2679586". Specifically, since oxetane compounds result in excellent heat resistance, adhesive properties, and chemical resistance, it is useful to simultaneously use these epoxy compounds which enhance reactivity.

[0010]

As an application example of the aforesaid technique, Japanese Patent Application Open to Public Inspection No. 2001-220526 discloses an application to ultraviolet radiation curable ink-jet printing. In recent years, the ultraviolet radiation curable ink-jet recording system, in which ink is cured by ultraviolet radiation, has received attention as an image forming method employing substrates with less ink absorbability.

[0011]

Generally, well known and used in practice as ultraviolet radiation curable ink is radically polymerizable ink. On the other hand, cationically polymerizable ink exhibits advantages such that polymerization inhibition due to oxygen, as found in the radically polymerizable ink, does not occur, low illuminance light sources are usable, unpleasant odors usually generated by acryl monomers are not formed, and components are low irritant, however, has not been put into practical use.

[0012]

Listed as reasons for not being in practical use are properties in which photosensitivity markedly decreases under high humidity and is temperature dependent. Ambience

dependent ink exhibits substantial problems in which its image quality varies depending on various ambience.

[0013]

Japanese Patent Application Open to Public Inspection No. 2002-137375 discloses a method in which cationically polymerizable ink is employed, and impinged ink is heated and subsequently exposed to radiation. However, from the viewpoint of printer cost and use of low heat resistant components, the use of heating mechanism seems to not be preferable. Further, Japanese Patent Application Open to Public Inspection No. 2001-181386 discloses 2-(4-methoxyphenyl)-3,3-dimethyloxetane as a compound to increase the reaction rate while employing oxetane compounds. Said compounds, when employed together with oxetane compounds such as di[1-ethyl(3-oxetanyl)]methyl ether and alicyclic epoxy compounds, exhibits reactivity which makes it possible to replace the alicyclic epoxy compounds. However, when low illuminance light sources such as a fluorescent lamp are employed, the resulting photosensitivity under high humidity ambience has not been sufficient.

[0014]

[PROBLEMS THEM PRESENT INVENTION INTENDS TO SOLVE]

From the viewpoint of the aforesaid problems, the present invention was achieved. An object of the present invention is to provide an oxetane compound capable of forming high quality images without bleeding, which exhibits excellent ink curability and close adhesion property to substrates, being not adversely affected by ambient humidity while even employing a low illuminance light source, an ink-jet ink capable of forming high quality images, and an image forming method using the aforesaid ink-jet ink.

[0015]

[MEANS TO SOLVE THE PROBLEMS]

The object of the present invention can be achieved by the following embodiments.

[0016]

1. An oxetane compound having an electron-donating group and an electron-withdrawing group in the molecule, and further having a substituent at the 2-position of the molecule.

[0017]

2. The oxetane compound of item 1, wherein the electron-donating group is substituted at the 2-position of the molecule and the electron-withdrawing group is substituted at the 4-position of the molecule.

[0018]

3. The oxetane compound of item 1 or item 2, having a substituent at the 3-position of the molecule.

[0019]

4. The oxetane compound of any one of items 1 to 3, wherein the oxetane compound has two or more oxetane groups in the molecule.

[0020]

5. An ink-jet ink comprising a photo-acid generating compound and the oxetane compound of any one of items 1 to 4.

[0021]

6. The ink-jet ink of item 5, wherein the oxetane compound has no substituent at the 2-position of the molecule.

[0022]

7. The ink-jet ink of item 5 or item 6, further comprising an epoxy compound or a vinyl ether compound.

[0023]

8. A method for forming an image, comprising the steps of:  
jetting a droplet of the ink-jet ink of any one of items 5 to 7 from an ink-jet head onto a recording material;  
and

irradiating the jetted droplet of the ink-jet ink with an active ray.

[0024]

In order to overcome the aforesaid problems, the inventors of the present invention performed diligent investigations. As a result, it was discovered that by using, in an ink-jet ink, oxetane compounds which were characterized in that an electron donating group as well as an electron attractive group was incorporated into the molecular structure and the 2-position was substituted, it was possible to prepare high quality images being not affected by ambient humidity even while employing low illuminance light sources. As a result, the present invention was realized.

[0025]

Further, in the present invention, when employed as oxetane compounds are multifunctional oxetane compounds, having at least two oxetane rings, in which the 2-position is substituted with an electron donating group, the 4-position is substituted with an electron attractive group and the 3-position has a substituent, it is possible to further enhance the effects of the present invention.

[0026]

In the present invention, by substituting the 2-position of oxetane compounds with an electron donating

group, the O-C distance of the oxetane ring increases to result in higher reactivity. Further, by substituting the 4-position with an electron attractive group, the oxetane structure is deformed to be unsymmetrical on the 2-position side and the 4-position side, whereby it becomes possible to have a structure resulting in higher reactivity.

[0027]

Further, by allowing the 3-position of oxetane compounds to have a substituent, when employed as an ink composition, it is possible to enhance compatibility with other compounds whereby by forming a multifunctional structure, it becomes possible to appropriately incorporate safety, hydrophobicity, viscosity, surface tension, and other physical parameters.

[0028]

By allowing for multifunctionality, it becomes possible to enhance the reaction rate as well as physical properties of cured layers.

[0029]

Further, in the ink-jet ink of the present invention, by using the oxetane compounds of the present invention together with oxetane compounds having no substituent at the 2-position, it becomes possible to achieve low viscosity

preferred for an ink-jet ink and also possible to enhance the reactivity as well as the cured layer strength. Still further, by using the oxetane compounds together with epoxy compounds or vinyl ether compounds, which are cationically polymerizable monomers usable in combination, it becomes possible to appropriately control physical properties of the resulting layers, close adhesion properties to substrates, and physical properties of the ink.

[0030]

The present invention will now be detailed.

The oxetane compounds of the present invention are characterized in that in the molecular structure, incorporated is an electron donating group as well as an electron attractive group, and the 2-position is substituted. Of these, preferred are multifunctional oxetane compounds, having at least two oxetane rings, in which the 2-position is substituted with an electron donating group, the 4-position is substituted with an electron attractive group, and the 3-position has a substituent.

[0031]

In the oxetane compounds of the present invention, an electron donating group, as described herein, refers to the substituent which results in a negative Hammett substituent



constant  $\sigma_p$  value. Examples of such compounds include  $-\text{NH}_3$  or alkyl (R) substituted  $-\text{NR}_3$ ,  $-\text{OH}$ ,  $-\text{OCH}_3$ , or an alkoxy group comprised of an alkyl group having at least two carbon atoms,  $-\text{NHCOCH}_3$  or an alkyl (R) substituted  $-\text{NRCOCR}_3$ ,  $-\text{C}_6\text{H}_5$ , a substituted type  $-\text{C}_6\text{H}_5$  described in Japanese Patent Application Open to Public Inspection No. 2001-181386,  $-\text{CH}_3$ , or an alkyl group having at least two carbon atoms, or a cyclic alkyl group such as a cyclohexyl group. Of these, preferred are structures having no basic N atom. The aforesaid basic N atom quenches protons which are active species of cationic polymerization, whereby photosensitivity decreases.

[0032]

On the other hand, an electron attractive group, as described herein, refers to the substituent which results in a positive Hammett substituent constant  $\sigma_p$  value. Specific examples of electron attractive groups include  $-\text{N}(\text{CH}_3)_3^+$ ,  $-\text{NO}_2$ ,  $-\text{CN}$ ,  $-\text{SO}_3\text{H}$ ,  $-\text{COOH}$ ,  $-\text{CHO}$ ,  $-\text{COR}$ ,  $-\text{X}$  (halogen),  $-\text{CX}_3$  or a halogenated alkyl group having at least two carbon atoms. Of these, preferred are  $-\text{COR}$ ,  $-\text{X}$ , and a halogenated alkyl group.

[0033]

Based on molecular calculation, it is possible to estimate to some extent the reactivity of oxetane in which the aforesaid electron donating group and electron attractive group are substituted at the 2-position and the 4-position, respectively. For example, the molecular calculation achieved by employing Mopac 3.0, manufactured by Fujitsu Ltd., shows that in the case of providing a proton onto the O atom of oxetane, as O-C bond distance increases, reactivity also increases.

[0034]

The following references can be applied to synthesize oxetane compounds having a substituent at the 2 or 4 position of the ring.

[0035]

- (1) Hu Xianming, Richard M. Kellogg, *Synthesis*, 533 - 538, May (1995)
- (2) A. O. Fitton, J. Hill, D. Ejane, R. Miller, *Synth.*, 12, 1140 (1987)
- (3) Toshiro Imai and Shinya Nishida, *Can. J. Chem.* Vol. 59, 2503 - 2509 (1981)
- (4) Nobujiro Shimizu, Shintaro Yamaoka, and Yuho Tsuno, *Bull. Chem. Soc. Jpn.*, 56, 3853 - 3854 (1983)
- (5) Walter Fisher and Cyril A. Grob, *Helv. Chim. Acta.*, 61,

2336 (1987)

- (6) Chem. Ber. 101, 1850 (1968)
- (7) "Heterocyclic Compounds with Three- and Four-membered Rings", Part Two, Chapter IX, Interscience Publishers, John Wiley & Sons, New York (1964)
- (8) Bull. Chem. Soc. Jpn., 61, 1653 (1988)
- (9) Pure Appl. Chem., A29 (10), 915 (1992)
- (10) Pure Appl. Chem., A30 (2 & amp;3), 189 (1993)
- (11) Japanese Patent Application Open to Public Inspection  
No. 6-16804
- (12) DE 10221858

Examples of synthesis employed the above-mentioned references are shown below. However, the present invention is not limited to the followings.

[0036]

(Synthesis Example 1)

Synthesis of Exemplified Compound 1: 3,3,4,4-tetramethyl-2,2-diphenyloxetane

A benzene solution containing benzophenone and 2,3-dimethyl-but-2-ene was placed in a photochemical reaction apparatus made of Pyrex (registered trade mark) into which argon gas was sealed, and while stirring, was exposed to ultraviolet radiation for 12 hours, employing a high pressure

mercury lamp. Subsequently, after removing the solvent, vacuum distillation was performed, whereby a targeted compound was obtained.

[0037]

(Synthesis Example 2)

Synthesis of Exemplified Compound 2: 3-(2-ethyl-hexyloxymethyl)-2,3,4,4-tetramethyl-oxetane

While stirring a 1-bromo-2-ethylhexyl solution of (2,2,3,4-tetramethyl-oxetane-3-yl and an aqueous potassium hydroxide solution, tetra-n-butylammonium bromide was dripped into it. After 24 hours, methylene chloride and water were added. Subsequently, an organic phase was washed with water, dehydrated by anhydrous magnesium sulfate, and filtered. After removing the solvent, vacuum distillation was performed, whereby a targeted compound was obtained.

[0038]

(Synthesis Example 3)

Synthesis of Exemplified Compound 3: 2-(2-ethyl-hexyloxy)-2,3,3,4,4-pentamethyl-oxetane

While stirring a 1-bromo-2-ethylhexyl solution of (2,3,3,4,4-pentamethyl-oxetane-2-ol and a aqueous potassium hydroxide solution, tetra-n-butylammonium bromide was dripped. After 24 hours, methylene chloride and water were

added. Subsequently, the organic phase was washed with water, dehydrated by anhydrous magnesium sulfate, and filtered. After removing the solvent, vacuum distillation was performed, whereby a targeted compound was obtained.

[0039]

(Synthesis Example 4)

Synthesis of Exemplified Compound 4: 4,4'-bis[(2,4-dimethyl-3-ethyl-3-oxetanyl)methoxy]biphenyl

While stirring, 3-chloromethyl-3-ethyl-2,4-dimethyl-oxetane, 4,4'-bisphenol, and tetrabutylphosphonium bromide were heated to 80 °C. An aqueous potassium hydroxide solution was dripped. The resulting mixture was heated to approximately 110 °C to start reflux. While refluxed, the reaction was allowed to proceed over 8 hours. After the reaction, the reaction mixture was cooled to room temperature. Subsequently, pure water was added and the resulting mixture was well stirred. Thereafter, deposits were collected by filtration. The resulting deposits were washed with water, followed by washing with methanol. Subsequently, drying was performed employing a vacuum dryer, whereby a targeted compound was obtained.

[0040]

(Synthesis Example 5)

Synthesis of Exemplified Compound 5: 1,7-bis(2,3,3,4,4-pentamethyl-oxetanyl)heptane

A mixture consisting of 2,12-diethyl-2,12-dimethyl-tridecane-1,3,11,13-tetraol, diethyl carbonate, and potassium carbonate was refluxed until the temperature decreased to less than 120 °C. While the resulting mixture was maintained at 80 - 82 °C, vacuum distillation was carried out, whereby a targeted compound was obtained.

[0041]

(Synthesis Example 6)

Synthesis of Exemplified Compound 6: oxetanyl silsesquioxanes

Isopropyl alcohol, an aqueous solution of hydroxydized tetramethylammonim, and water were charged. Thereafter, the oxetane compound, described below, was gradually added and the resulting mixture was allowed to stand at room temperature while stirring for 24 hours. After the reaction, toluene was added to the reaction system and the resulting reaction solution was washed with a saturated sodium chloride solution. Subsequently, washing was repeated until the water layer in the separating funnel became neutral. Subsequently, the organic layer was collected and dehydrated by anhydrous

sodium sulfate. Thereafter, toluene was distilled out under vacuum, whereby a targeted compound was obtained.

[0042]

Further, each synthetic example, described above, relates to an example of the compound in which an electron donating group is substituted at either the 2-position or the 4-position. Such a compound is useful due to high reactivity to oxetane compounds which have no substituent at either the 2-position or the 4-position.

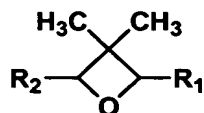
[0043]





In the present invention, it is preferable that the aforesaid oxetane compounds, which are substituted with an electron attractive group at the 4-position, are further substituted with an electron donating group at the 2-position. It is possible to synthesize oxetane compounds substituted with an electron attractive group, employing the same method as above.

[0044]

Specific examples of oxetane compounds, having an electron donating group at the 2-position as well as an electron attractive group at the 4-position, are shown below. However, the present invention is not limited thereto.

[0045]



|                         | R <sub>1</sub>                                                                                        | R <sub>2</sub>    |
|-------------------------|-------------------------------------------------------------------------------------------------------|-------------------|
| Exemplified Compound 7  | —OCH <sub>3</sub>                                                                                     | CF <sub>3</sub>   |
| Exemplified Compound 8  | —O—                  | CF <sub>3</sub>   |
| Exemplified Compound 9  |  —OCH <sub>3</sub>   | CF <sub>3</sub>   |
| Exemplified Compound 10 | —CH <sub>3</sub>                                                                                      | CF <sub>3</sub>   |
| Exemplified Compound 11 |  —OCH <sub>3</sub>  | CF <sub>2</sub> H |
| Exemplified Compound 12 |  —OCH <sub>3</sub> | CFH <sub>2</sub>  |

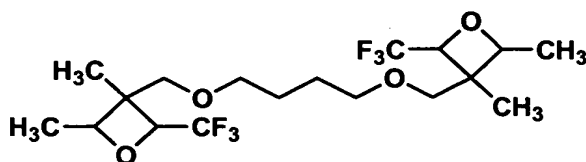
[0046]

Further, compounds having at least two oxetane groups in the molecule may be provided with multifunction via the 3-position, or either the 2-position or the 4-position of the aforesaid compounds. A specific example of a compound having at least two oxetane groups are shown below. However, the present invention is not limited thereto.



[0047]

## Exemplified Compound 13



[0048]

In the oxetane compounds of the present invention, it is preferable that the 3-position has a substituent. Further, it is possible to synthesize the oxetane compounds according to the present invention by following the procedures described in the aforesaid Publications H - L. Further, it is possible to provide multifunctionality to Exemplified Compounds 8 - 13 in the same manner as the method described in General Formulas (7) - (9).

[0049]

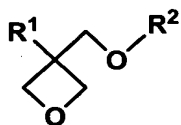
In the ink-jet ink of the present invention, it is preferable to use an oxetane compound having an electron donating group as well as an electron attractive group in the molecules and having no substituent at the 2-position, together with an oxetane compound having no substituent at the 2-position, since it is possible to dramatically increase the photosensitivity and achieve desired curing in an ambience of high humidity.

[0050]

As oxetane compounds having no substituent at the position 2, the compounds shown by the following General Formula (1) are listed.

[0051]

General Formula (1)



[0052]

In the General Formula (1),  $R^1$  is a hydrogen atom, alkyl group having 1 - 6 carbon atoms such as methyl group, ethyl group, propyl group or butyl group, fluoro-alkyl group having 1 to 6 carbon atoms, allyl group, aryl group, furyl group, or thienyl group.  $R^2$  is an alkyl group having 1 to 6 carbon atoms such as methyl group, ethyl group, propyl group or butyl group; alkenyl group having 2 to 6 carbon atoms such as 1-propenyl group, 2-propenyl group, 2-methyl-1-propenyl group, 2-methyl-2-propenyl group, 1-butenyl group, 2-butenyl group or 3-butenyl group; a group having aromatic ring such as phenyl group, benzyl group, fluoro-benzyl group, methoxy-benzyl group or phenoxy-ethyl group; alkyl carbonyl group having 2 to 6 carbon atoms such as ethyl carbonyl group,

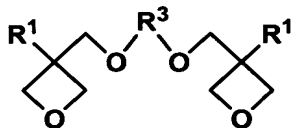
propyl carbonyl group or butyl carbonyl group; alkoxy carbonyl group having 2 to 6 carbon atoms such as ethoxy carbonyl group, propoxy carbonyl group or butoxy carbonyl group; N-alkyl carbamoyl group having 2 to 6 carbon atoms such as ethyl carbamoyl group, propyl carbamoyl group, butyl carbamoyl group or pentyl carbamoyl group. As the oxetane compound used in the present invention, it is particularly preferable that the compound having one oxetane ring is used, because the obtained composition is excellent in the coking property, and the operability is excellent in the low viscosity.

[0053]

Next, as the compound having two oxetane rings, the compounds shown by the following General Formula (2) are listed.

[0054]

General Formula (2)



[0055]

In the General Formula (2),  $R^1$  is the same group as the group shown in the above-described General Formula (1).  $R^3$

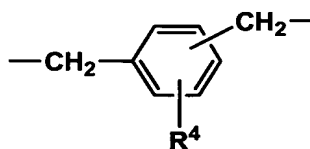
is, for example, a linear or branching alkylene group such as ethylene group, propylene group or butylene group; linear or branching poly (alkylene-oxy) group such as poly (ethylene oxy) group or poly (propylene oxy) group; linear or branching un-saturated hydrocarbon group such as propenylene group, methyl propenylene group or butenylene group; carbonyl group; alkylene group including carbonyl group; alkylene group including carboxyl group; alkylene group including carbamoyl group.

[0056]

Further,  $R^3$  may also be a polyhydric group selected from the group shown by the following General Formulas (3), (4) and (5).

[0057]

General Formula (3)



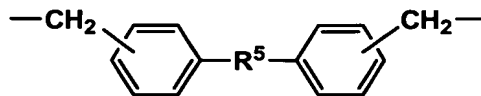
[0058]

In the General Formula (3),  $R^4$  is a hydrogen atom, an alkyl group having 1 to 4 carbon atoms such as methyl group, ethyl group, propyl group or butyl group, or alkoxy group having 1 to 4 carbon atoms such as methoxy group, ethoxy

group, propoxy group or butoxy group, or halogen atom such as chloride atom or bromine atom, nitro group, cyano group, mercapto group, lower alkyl carboxyl group such as the group having 1 to 5 carbon atoms, carboxyl group, or carbamoyl group.

[0059]

General Formula (4)

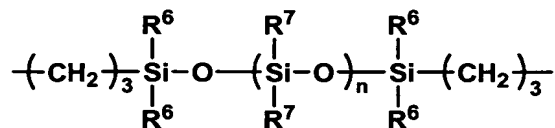


[0060]

In the General Formula (4),  $R^5$  is oxygen atom, sulfide atom, methylene group,  $\text{---NH---}$ ,  $\text{---SO---}$ ,  $\text{---SO}_2\text{---}$ ,  $\text{---C(CF}_3)_2\text{---}$ , or  $\text{---C(CH}_3)_2\text{---}$ .

[0061]

General Formula (5)



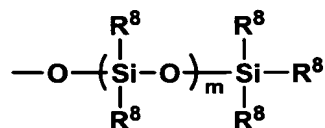
[0062]

In the General Formula (5),  $R^6$  is an alkyl group having 1 to 4 carbon atoms such as methyl group, ethyl group, propyl group or butyl group, or aryl group. Numeral  $n$  is an integer of 0 - 2000.  $R^7$  is an alkyl group having 1 to 4 carbon atoms such as methyl group, ethyl group, propyl group or butyl

group, or aryl group.  $R^7$  is also a group selected from the group shown by the following General Formula (6).

[0063]

General Formula (6)



[0064]

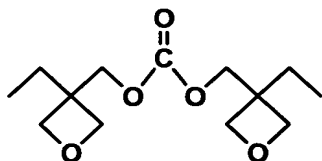
In the General Formula (6),  $R^8$  is an alkyl group having 1 to 4 carbon atoms such as methyl group, ethyl group, propyl group or butyl group, or aryl group. Numeral  $m$  is an integer of 0 - 100.

[0065]

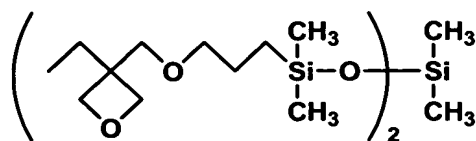
As a specific example of the compound having 2 oxetane rings, the compounds shown by the following structural formulas are listed.

[0066]

Exemplified compound 14



Exemplified compound 15



[0067]

Exemplified compound 14 shown by the above structural formula is a compound in which  $R^1$  is an ethyl group, and  $R^3$  is a carboxy group in General Formula (2).

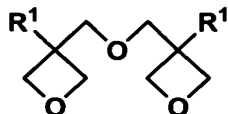
Exemplified compound 15 shown by the above structural formula is a compound in which each  $R^6$  and  $R^7$  are a methyl group, and  $n$  is 1 General Formula (5).

[0068]

Among the compound having 2 oxetane rings, as a preferable example except for the above-described compounds, there are compounds shown by the following General Formula (7). In the General Formula (7),  $R^1$  is the same group as in the General Formula (1).

[0069]

General Formula (7)

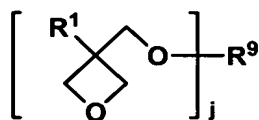


[0070]

As the compounds having 3 - 4 oxetane rings, the compounds shown in the following General Formula (8) are listed.

[0071]

General Formula (8)

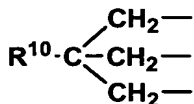


[0072]

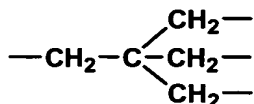
In the General Formula (8),  $\text{R}^1$  is the same group as in the General formula (1).  $\text{R}^9$  is, for example, branching alkylene group having 1 to 12 carbon atoms such as groups shown by the following General Formulas (9), (10), branching poly(alkylene oxy) group such as group shown by the following General Formula (11), or branching polysiloxane group such as group shown by the following General Formula (12) is listed. Numeral  $j$  is 3 or 4.

[0073]

A

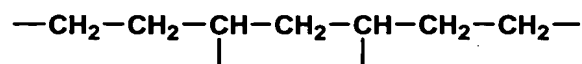


B

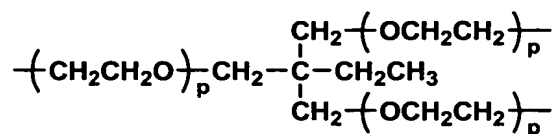




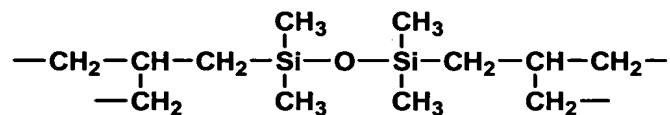
C



D



E



[0074]

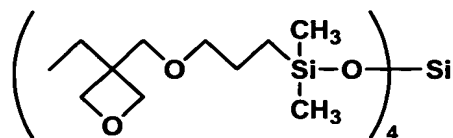
In Formula A, R<sup>10</sup> is a lower alkyl group such as a methyl, ethyl, or propyl group. In Formula D, p is an integer of 1 to 10.

[0075]

As the specific example of the compound having 3 to 4 oxetane rings, the compound shown in the following Exemplified compound 10 is cited.

[0076]

Exemplified compound 16

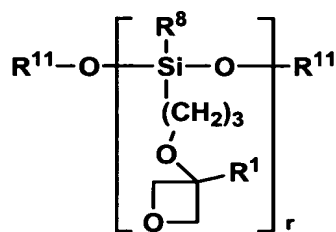


[0077]

Furthermore, as an example of the compounds having 1 - 4 oxetane rings except the above examples, there are compounds shown in the following General Formula (9).

[0078]

General Formula (9)



[0079]

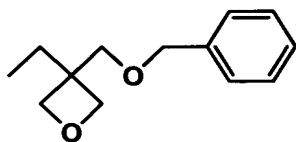
In the General Formula (9), R<sup>1</sup> is the same group as in General Formula (1) and R<sup>8</sup> is the same group as in the General Formula (6). R<sup>11</sup> is alkyl group having 1 to 4 carbon atoms such as methyl group, ethyl group, propyl group or butyl group, or tri-alkyl silyl group, and numeral r is 1 - 4.

[0080]

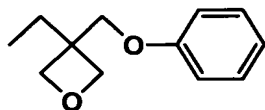
As preferable specific examples of the oxetane compounds used in the present invention, there are compounds shown below.

[0081]

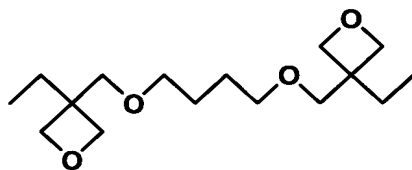
Exemplified compound 17



Exemplified compound 18



Exemplified compound 19

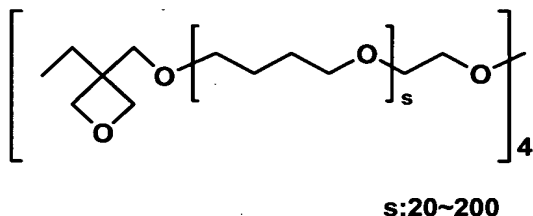
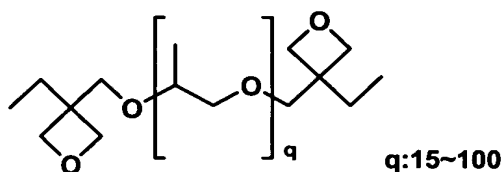
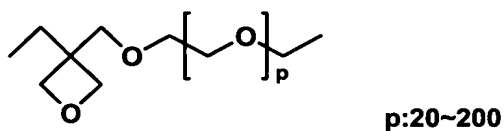


[0082]

The production method of the compounds having the oxetane ring is not particularly limited, and it may be conducted according to the conventionally known method, and for example, there is a synthetic method of an oxetane ring from diol disclosed by Pattison (D. B. Pattison, J. Am. Chem. Soc., 3455, 79 (1957)).

Further, other than them, compounds having 1 - 4 oxetane rings, which have high molecular weight of molecular weight of about 1000 - 5000, are also listed. As an example of them, for example, the following compounds are listed.

[0083]



[ 0084 ]

The ink-jet ink of the present invention preferably incorporate an oxetane compound with an epoxy compound or a vinyl compound. The oxetane compound has an electron donating group and an electron withdrawing group in the molecule, and at the same time being substituted at the 2 position of the ring.

[0085]

(Epoxy compound)

Among epoxy compounds, referable aromatic epoxy compounds are di- or poly-glycidyl ether, which is

synthesized by the reaction of polyhydric phenol having at least one aromatic core or alkylene oxide-added polyhydric phenol and epichlorohydrin, and for example, di- or poly-glycidyl ether of bisphenol A or of alkylene oxide-added bisphenol A, di- or poly-glycidyl ether of hydrogenated bisphenol A or of alkylene oxide-added hydrogenated bisphenol A, and novolak type epoxy resin, are listed. Herein, as alkylene oxide, ethylene oxide and propylene oxide are listed.

[0086]

As alicyclic epoxide, a cyclohexene oxide or cyclopentene oxide, which is obtained by epoxidation of the compound having cycloalkane ring such as at least one cyclohexene or cyclopentene ring by the appropriate oxidant such as hydrogen peroxide or peracid, is preferable.

[0087]

As a preferable aliphatic epoxide, there is di- or poly-glycidyl ether of aliphatic polyvalent alcohol or of alkylene oxide-added aliphatic polyvalent alcohol, and as its representative example, di-glycidyl ether of alkylene glycol such as di-glycidyl ether of ethylene glycol, di-glycidyl ether of propylene glycol and glycidyl ether of 1, 6-hexane diol, poly-glycidyl ether of polyvalent alcohol such as di-or

tri-glycidyl ether of glycerin or of alkylene oxide added glycerin, and di-glycidyl ether of polyalkylene glycol such as di-glycidyl ether of polyethylene glycol or of alkylene oxide-added polyethylene glycol, and di-glycidyl ether of polypropylene glycol or of alkylene oxide-added polypropylene glycol, are listed. Herein, as alkylene oxide, ethylene oxide and propylene oxide are listed.

[0088]

In these epoxides, when the quick hardening ability is considered, aromatic epoxide and alicyclic epoxide are preferable, and particularly, alicyclic epoxide is preferable. In the present invention, on kind of the above epoxides may be solely used, and more than 2 kinds of them may also be used by appropriately being combined.

[0089]

(Vinyl ether compound)

Also as a vinyl ether compound preferably used in the ink of the present invention, publicly known vinyl ether compounds can be used, and for example, di or tri-vinyl ether compound, such as ethylene glycol di-vinyl ether, di-ethylene glycol di-vinyl ether, tri-ethylene glycol di-vinyl ether, propylene glycol di-vinyl ether, di-propylene glycol di-vinyl ether, butane diol di-vinyl ether, hexane diol di-vinyl

ether, cyclohexane di-methanol di-vinyl ether, tri-methylol propane tri-vinyl ether, or mono vinyl ether compound, such as ethyl vinyl ether, n-butyl vinyl ether, iso-butyl vinyl ether, octadecyl vinyl ether, cyclohexyl vinyl ether, hydroxy butyl vinyl ether, 2-ethyl-hexyl vinyl ether, cyclo-hexane di-methanol mono-vinyl ether, n-propyl vinyl ether, iso-propyl vinyl ether, iso-propenyl ether-o-propylene carbonate, dodecyl vinyl ether, or di-ethylene glycol mono vinyl ether vinyl ether, is listed.

[0090]

In these vinyl ether compounds, when the hardenability, adhesion or surface hardness is considered, di or tri-vinyl ether compound is preferable, and particularly di-vinyl ether compound is preferable. In the present invention, one kind of the above vinyl ether compounds may also be used, and more than two kinds of them may also be used by being appropriately combined.

[0091]

One of the features of the ink-jet ink of the present invention is that the ink-jet ink incorporates an oxetane compound with a photo-acid generating agent, the oxetane compound having an electron donating group and an electron

withdrawing group in the molecule and at the same time being substituted at the 2 position of the ring.

[0092]

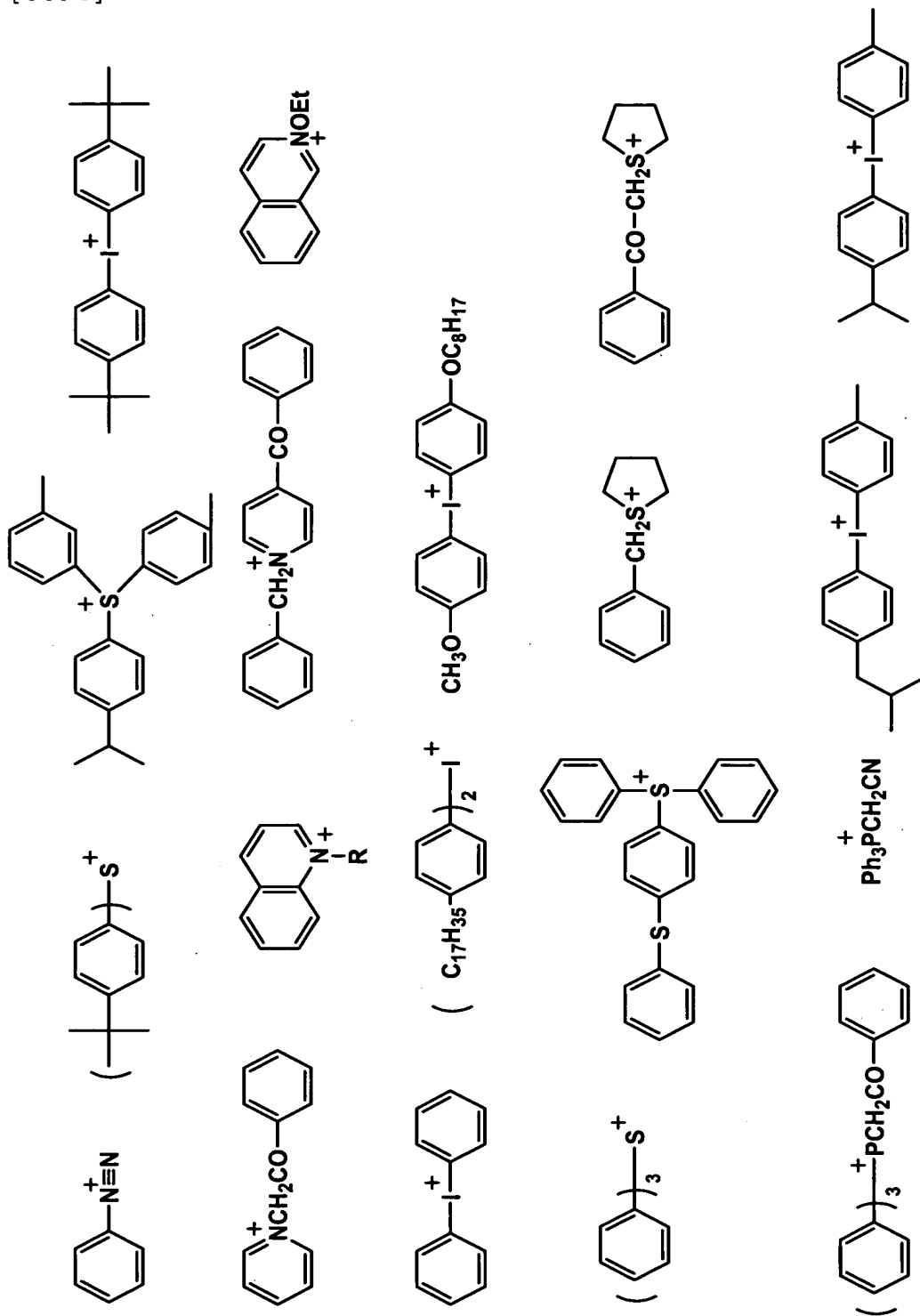
As the photo initiator, all publicly known photo acid generators (a compound which generates the acid by the active ray, such as ultraviolet rays) can be used. As the photo acid generator, for example, a chemical amplification type photo resist or compound used for the light cationic polymerization is used (Organic electronics material seminar "Organic material for imaging" from Bunshin publishing house (1993), refer to page 187 - 192). Examples preferable for the present invention will be listed below.

[0093]

Firstly, aromatic onium compound  $B(C_6F_5)_4^-$ ,  $PF_6^-$ ,  $AsF_6^-$ ,  $SbF_6^-$ ,  $CF_3SO_3^-$  salt, such as diazonium, ammonium, iodonium, sulfonium, phosphonium, can be listed. Specific examples of the onium compounds will be shown below.



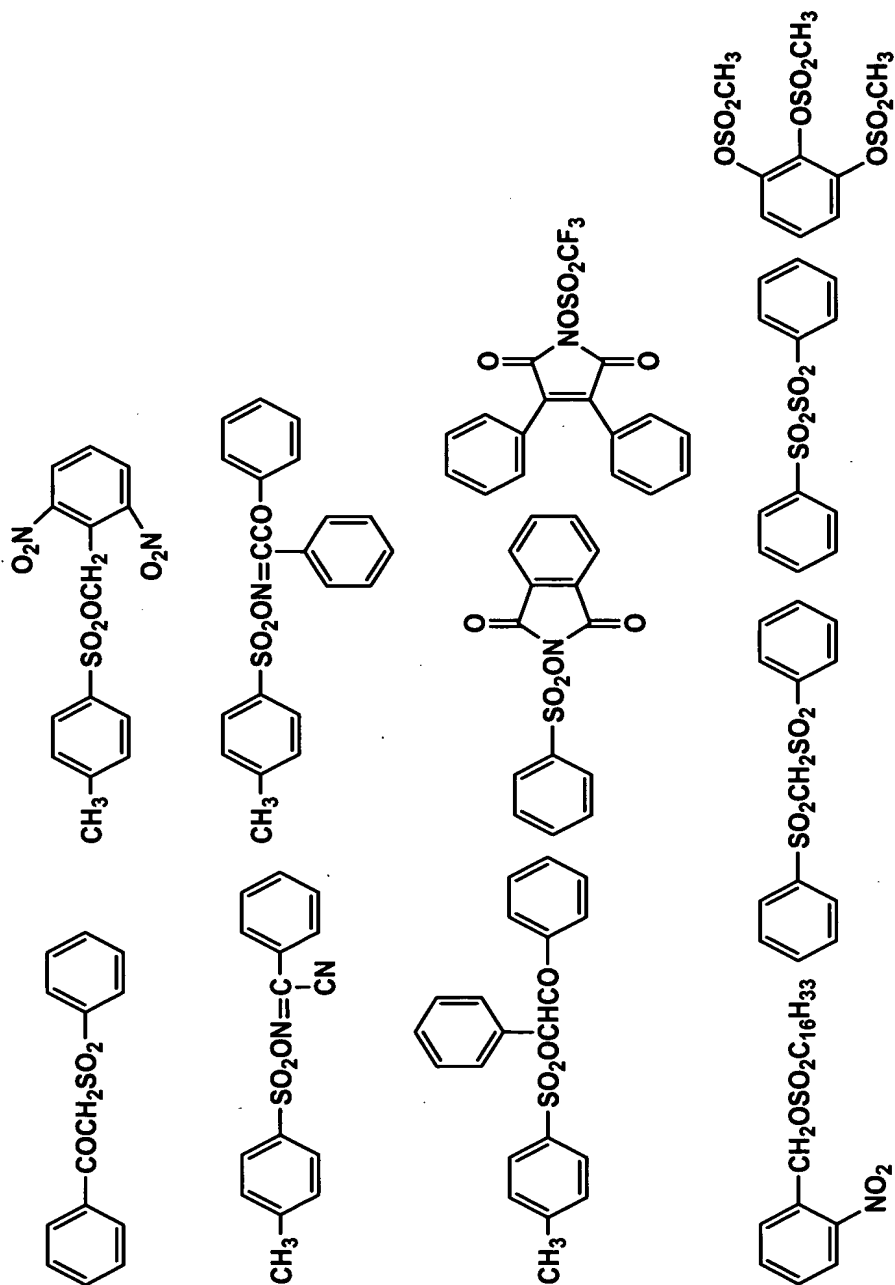
[ 0094 ]



[0095]

Secondly, sulfone compounds, which generate sulfonic acid, can be listed. Examples of specific compounds will be shown below.

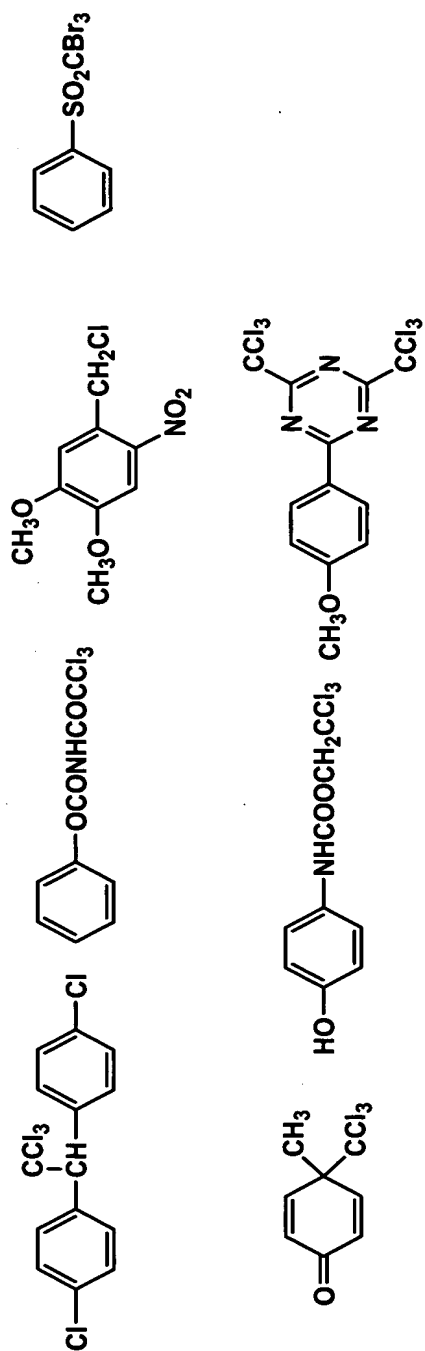
[0096]



[0097]

Thirdly, halogenide which generates hydrogen halide can also be used. Examples of specific compounds will be shown below.

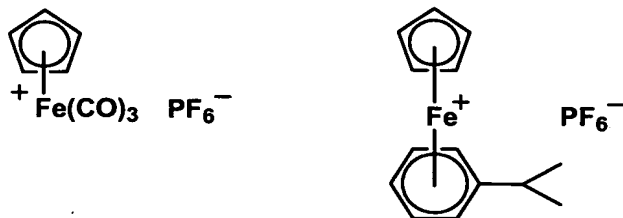
[0098]



[0099]

Fourthly, ferrite allene complex can be listed.

[0100]



[0101]

Other than above, other additives can be used in the ink-jet ink of the present invention.

[0102]

As the colorants in the present invention are, the colorants, which can be solved or dispersed in main component of the polymeric compound, can be used, however, from the viewpoint of weather fastness, the pigment is preferable.

[0103]

As the pigment, the followings can be used, however, it is not limited to these.

C.I. Pigment Yellow-1, 3, 12, 13, 14, 17, 81, 83, 87, 95, 109, 42,

C. I. Pigment Orange-16, 36, 38,

C. I. Pigment Red-5, 22, 38, 48:1, 48:2, 48:4, 49:1, 53:1, 57:1, 63:1, 144, 146, 185, 101,

C. I. Pigment Violet-19, 23,

C. I. Pigment Blue-15:1, 15:3, 15:4, 18, 60, 27, 29,

C. I. Pigment Green-7, 36

C. I. Pigment White-6, 18, 21,

C. I. Pigment Black-7.

To disperse the pigment, a ball mill, sand mill, attritor, roll mill, agitator, Henschel mixer, colloid mill, ultrasonic homogenizer, Pearl mill, wet jet mill, or paint shaker may be used. Further, when the pigment is dispersed, the dispersing agent can also be added. It is preferable that, as the dispersing agent, high polymeric dispersing agent is used. As the high polymeric dispersing agent, Solsperser series of Avesco co., is cited.

Further, as the dispersion auxiliary agent, the synergist corresponding to each kind of pigment can also be used. It is preferable that 1 - 50 parts by weight of these dispersing agent and dispersion auxiliary agent are added to 100 parts by weight of the pigment. The dispersion medium is solvent or polymeric compound, and it is preferable that the ultraviolet ray-curable ink used in the present invention comprises no-solvent, because it is reacted and hardened just after the arrival of the ink. When the solvent remains in the hardened image, the problem of deterioration of

solvent resistance and VOC (Volatile Organic Compound) of the remained solvent is raised. Accordingly, it is preferable in the dispersion aptitude that the dispersion medium is not solvent, but polymeric compounds, and the monomer in which the viscosity is lowest in them, is selected.

[0104]

When the dispersion is conducted, it is preferable to configure the pigment, dispersing agent, selection of diluent for the dispersion so that average particle size of the pigment become 0.08 - 0.5  $\mu\text{m}$ , more preferably 0.3 - 10  $\mu\text{m}$ , still more preferably, 0.3 - 3  $\mu\text{m}$ . By this particle size control, the nozzle plugging of the ink-jet head is suppressed, and the preservation stability of the ink, ink transparency and hardening sensitivity can be maintained.

[0105]

It is preferable for the colorant that the addition amount is 1 weight% to 10 weight% of the whole of the ink.

(The other components)

In order to increase the keeping quality of the ink components, the polymerization inhibitor of 200 - 20000 ppm can be added. Because it is preferable that the ultraviolet ray-curable ink is heated and made to low viscosity, and



jettied, it is preferable for preventing the head from plugging by the thermal polymerization that the polymerization inhibitor is added. As the polymerization inhibitor, for example, a basic compound can be added.

[0106]

In the present invention, for the purpose of enhancing stable ejection as well as stable storage, it is also possible to employ thermal base generating agents.

[0107]

Preferably employed as thermal base generating agents are, for example, salts of an organic acid and a base which thermally decompose to result in decarboxylation, amine releasing compounds upon being decomposed by reaction such as intramolecular nucleophilic substitution reaction, Lossen rearrangement, and Beckmann rearrangement, and base releasing compounds which undergo various reactions when heated. Specific examples include trichloroacetic acid salts described in British Patent No. 998,949, alpha-sulfonylacetic acid salts described in U.S. Patent No. 4,060,420, propyl acid salts described in Japanese Patent Publication Open to Public Inspection No. 59-157637, 2-carboxycarboxamide derivatives, basic components described in Japanese Patent Publication Open to Public Inspection No. 59-168440, organic bases, and

alkali metals, salts of thermally decomposable acids employing alkaline earth metals, hydroxamcarbamate utilizing the Lossen rearrangement described in Japanese Patent Publication Open to Public Inspection No. 59-180537 and aldoximecarbamates described in Japanese Patent Publication Open to Public Inspection No. 59-195237 which thermally form nitryl. Other than these, thermal base generating agents are useful which are described in British Patent No. 998,945, U.S. Patent No. 3,220,846, and British Patent No. 279,480, Japanese Patent Publication Open to Public Inspection Nos. 50-22625, 61-32844, 61-51139, 61-52638, 61-51140, 61-53634 - 61-53640, 61-55644, and 61-55645. More specific examples include trichloroacetic acid guanidine, trichloroacetic acid methyl guanidine, potassium trichloroacetate, phenylsulfonylacetic acid guanidine, p-chlorophenylsulfonylacetic acid guanidine, p-methanesulfonylphenylsulfonylacetic acid guanidine, potassium phenylpropiol acetate, phenylpropionic acid guanidine, cesium phenylpropiolate, p-chlorophenolpropionic acid guanidine, p-phenylene-bis-phenylpropionic acid guanidine, phenylsulfonyl acetic acid tetramethylammonium, and phenylpropionic acid tetramethylammonium. It is possible to use the aforesaid thermal base generating agents in the wide range.

[0108]

The ink of the present invention may contain acid increasing agents, known in the art by Japanese Patent Application Open to Public Inspection Nos. 8-248561 and 9-341106, which generate acid, employing acid generated by exposure of actinic radiation.

[0109]

In the present invention, the surface tension of the ink is preferably in the range of 25 - 40 mN/m at 25 °C. When the surface tension of the ink is less than 25 mN/m at 25 °C, it is difficult to achieve stable ink ejection. On the other hand, when it exceeds 40 mN/m, it is extremely difficult to result in the desired dot diameter.

[0110]

In order to adjust the surface tension, if desired, surface active agents may be incorporated. Examples of surface active agents which are preferably employed in the present invention include anionic surface active agents such as dialkylsulfosuccinic acid salts, alkyl naphthalenesulfonic acid salts, and fatty acid salts; nonionic surface active agents such as polyoxyethylene alkyl ethers, polyoxyethylene alkyl allyl ethers, acetylene glycols, polyoxyethylene-polyoxypropylene block copolymers; cationic surface active

agents such as alkylamine salts and quaternary ammonium salts; and surface active agents having a polymerizable group. Of these, specifically preferred are surface active agents having a polymerizable group such as silicon modified acrylate, fluorine modified acrylate, silicon modified epoxy, fluorine modified epoxy, silicon modified oxetane, and fluorine modified oxetane.

[0111]

Other than that, corresponding to the necessity, the surfactant, leveling additive agent, mat agent, polyester resin for adjusting the film property, polyurethane resin, vinyl resin, acrylic resin, rubber resin, or wax can be added. In order to improve the adhesion to the recording medium, it is also effective that the very fine amount of organic solvent is added. In this case, the addition within the range that the problem of the solvent resistance or VOC is not generated, is effective, and the amount is 0.1 - 5 weight%, preferably 0.1 - 3 weight% of total ink weight.

[0112]

In the image forming method of the present invention, an ink composition is ejected onto a recording material to form images. Subsequently, the resulting ink composition is

exposed to actinic radiation such as ultraviolet radiation to cure the ink.

[0113]

In the image forming method of the present invention, it is preferable to decrease the viscosity of a liquid ink composition by heating the liquid ink composition as well as the nozzle(s) during ink ejection. The heating temperature is commonly 30 - 80 °C, but is preferably 35 - 60 °C.

[0114]

In the present invention, the thickness of the total ink layer after curing while exposed to actinic radiation is preferably 2 - 20  $\mu\text{m}$ . In the actinic radiation curable ink-jet recording in the screen printing field, at present, the ink layer thickness exceeds 20  $\mu\text{m}$ . As a result, the aforesaid ink-jet recording is not applicable to the soft package printing field due to the following. Since thin plastic materials are frequently used as a recording material, the aforesaid problems of curling as well as wrinkling occur. In addition, the stiffness and feel of quality of the entire printed materials are adversely affected. In the present invention, the volume of a liquid droplet ejected from each nozzle is preferably 2 - 15 pl.

[0115]

In the present invention, in order to enable formation of highly detailed images, it is preferable that exposure duration is as short as possible. However, in the present invention, it is preferable to initiate radiation exposure at the time when either the ink viscosity or the water content ratio reaches the desired value.

[0116]

In more detail, as to the radiation exposure conditions, it is preferable to initiate actinic radiation exposure 0.001 - 2.0 seconds after ink impingement, and is more preferably to initiate it 0.001 - 0.4 second. Further, it is preferable to finish the exposure after 0.1 - 3.0 seconds, preferably within 0.2 - 1.0 second, so that radiation exposure is carried out at a level in which ink fluidity is almost lost. By setting the conditions as above, it is possible to minimize the increase in dot diameter as well as bleeding between dots.

[0117]

Disclosed as actinic radiation exposure methods is a basic method in Japanese Patent Application Open to Public Inspection No. 60-132767. According to the aforesaid patent, light sources are arranged on both sides of a recording head

unit, and the recording head as well as the light sources is scanned employing a shuttle system. Exposure is performed a definite time after ink impingement. Further, curing is finished employing another light source which is not driven. U.S. Patent No. 6,145,979 discloses a method in which optical fibers are employed as an exposure method and in addition, a method in which UV radiation is exposed to a recording section while collimated radiation is incident to a mirror's surface provided on the side surface of a recording head unit. In the image forming method of the present invention, the above methods are available.

[0118]

Further, the following method is also one of the preferable embodiments. Actinic radiation exposure is divided into two steps. Initially, while employing the aforesaid method, actinic radiation is exposed between 0.001 - 2.0 seconds after ink impingement. After finishing all printing, further the resulting printing is exposed to actinic radiation. By dividing actinic radiation exposure into two steps, it is possible to minimize contraction of recording materials which occurs during curing the ink.

[0119]

Examples of light sources employed in actinic radiation exposure include high pressure mercury lamps, metal halide lamps, non-electrode UV lamps, low pressure mercury lamps, UV lasers, xenon flash lamps, insectivorous lamps, black-light lamps, insecticide lamps, cold cathode tubes, and LEDs. The aforesaid light sources are not limited to these examples. However, of these, fluorescent tubes are preferred due to low energy consumption as well as low cost. From the viewpoint of sensitivity, preferred are radiation sources which emit radiation at a wavelength of 250 - 370 nm, and preferably having an emission peak of 270 - 320 nm. The illuminance is preferably 1 - 3,000 W/cm<sup>2</sup>, and is more preferably 1 - 200 W/cm<sup>2</sup>.

[0120]

As supports for the present invention, various types of non-absorptive supports can be used other than common coated paper and non-coated paper. Among them, preferably used are non-absorptive supports.

[0121]

Examples of non-absorptive supports are various types of plastic films including PET (polyethylene terephthalate) film, OPS (oriented polystyrene) film, OPP (oriented polypropylene) film, ONY (oriented nylon) film, PVC



(polyvinyl chloride) film, PE film, and TAC film. Employed as other plastic films may be polycarbonate, acrylic resins, ABS, acetal, PVA, and rubber. Further, metal and glass may also be employed.

Of these recording materials, when images are formed specifically on PET film, OPS film, OPP film, ONy film, or PVC film which are thermally shrinkable, the effects of the present invention are more pronounced. These substrates tend to curl and deform due to contraction during ink curing and heat generated during the curing reaction. In addition, it is difficult for the ink layer to keep up with contraction of the aforesaid substrate.

[0122]

The surface energy values of the aforementioned plastic films different from each other. It has been a problem that a dot diameter after ink-jetting varies depending on the recording materials. The preferred composition of the present invention includes OPP film and OPS film having a low surface energy and PET film having a relatively large surface energy. The preferred supports have a wettability index of 40 to 60 mN/m.

[0123]

In the present invention, from the viewpoint of the cost of recording materials such as packaging cost as well as production cost, print production efficiency, and compatibility with prints of various sizes, it is more advantageous to use long (web) recording materials.

[0124]

[EXAMPLES]

The present invention will now be described with reference to examples. However, the embodiments of the present invention are not limited thereto.

[0125]

<<Preparation of Ink-jet Ink>>

(Preparation of Magenta Ink 1)

Magenta Ink 1 comprised of the composition described below was prepared as follows. A mixture of components except for a photolytically acid generating agent was dispersed for 4 hours, employing a sand grinder. Thereafter, the photolytically acid generating agent was added. After filtering the resulting mixture employing a 0.8  $\mu\text{m}$  pore membrane filter, vacuum dehydration was carried out while heated to 50 °C, whereby Magenta Ink 1 was prepared.

[0126]

C.I. Pigment Red 184

3 weight parts

|                                  |                  |
|----------------------------------|------------------|
| Oxetane compound (Exemplified    |                  |
| Compound 9)                      | 100 weight parts |
| Solsperse 24000 (manufactured by |                  |
| Avecia)                          | 1 weight part    |
| UVI-6990 (photolytically acid    |                  |
| generating agent, manufactured   |                  |
| by Dow Chemicals)                | 5 weight parts   |

(Preparation of Magenta Ink 2)

Magenta Ink 2 was prepared in the same manner as aforesaid Magenta Ink 1, except that the composition was varied as described below.

[0127]

|                                    |                 |
|------------------------------------|-----------------|
| C.I. Pigment Red 184               | 3 weight parts  |
| Oxetane compound (Exemplified      |                 |
| Compound 9)                        | 30 weight parts |
| Aron oxetane OXT-221 (manufactured |                 |
| by TOAGOSEI Co., Ltd.)             | 30 weight parts |
| Aron oxetane OXT-211 (manufactured |                 |
| by TOAGOSEI Co., Ltd.)             | 20 weight parts |
| Celoxide 2021P (manufactured by    |                 |
| Daiseru UCB)                       | 20 weight parts |
| Solsperse 24000 (manufactured by   |                 |
| Avecia)                            | 1 weight part   |

UVI-6990 (photolytically acid  
generating agent, manufactured  
by Dow Chemicals) 5 weight parts  
(Preparation of Magenta Ink 3)

Magenta Ink 3 was prepared in the same manner as  
aforesaid Magenta Ink 1, except that the composition was  
varied as described below.

[0128]

C.I. Pigment Red 184 3 weight parts  
Oxetane compound (Exemplified  
Compound 9) 50 weight parts  
Aron oxetane OXT-221 (manufactured  
by TOAGOSEI Co., Ltd.) 50 weight parts  
Solsperse 24000 (manufactured by  
Avecia) 1 weight part  
UVI-6990 (photolytically acid  
generating agent, manufactured  
by Dow Chemicals) 5 weight parts  
(Preparation of Magenta Ink 4)

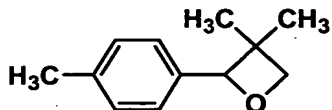
Magenta Ink 4 was prepared in the same manner as  
aforesaid Magenta Ink 1, except that the composition was  
varied as described below.

[0129]

|                                                                                      |                 |
|--------------------------------------------------------------------------------------|-----------------|
| C.I. Pigment Red 184                                                                 | 3 weight parts  |
| Oxetane Compound A                                                                   | 50 weight parts |
| Aron oxetane OXT-221 (manufactured<br>by TOAGOSEI Co., Ltd.)                         | 50 weight parts |
| Solsperse 24000 (manufactured by<br>Avecia)                                          | 1 weight part   |
| UVI-6990 (photolytically acid<br>generating agent, manufactured<br>by Dow Chemicals) | 5 weight parts  |

[0130]

Oxetane Compound A



[0131]

## &lt;&lt;Ink-jet Image Recording and Evaluation&gt;&gt;

By employing each of the magenta inks prepared as above, image recording as well as evaluation of the resulting images was carried according to the methods described below.

[0132]

(Image Evaluation A)

(Image Recording)

Each of the magenta inks prepared as above was ejected onto a polyethylene terephthalate film substrate, which had

been subjected to corona discharge treatment, employing piezo type ink-jet nozzles (having a nozzle pitch of 360 dpi; dpi, as described in the present invention, refers to the number of dots per inch or 2.54 cm) capable of forming a droplet volume of 7 pi, while heating the nozzle section to 50 °C, whereby a solid magenta image and 6-point MS Ming-cho type characters were printed. Employed as a light source was a fluorescent tube having a 308 nm peak. While adjusting the illuminance on the substrate surface below the light source at 10 mW/cm<sup>2</sup>, exposure was initiated 0.2 second and completed 0.7 second after ink impingement. Incidentally, the exposure energy was 5 mJ/cm<sup>2</sup>. The aforesaid image printing was performed at a low humidity ambience (25 °C and 20 percent relative humidity) as well as at a high humidity ambience (25 °C and 80 percent relative humidity).

[0133]

(Image Evaluation)

Each image prepared as above was subjected to the evaluation described below.

[0134]

<Evaluation of Ink Curability>

The ink curability of each of the images printed under different ambiances was evaluated based on the criteria below.

[0135]

A: No tackiness was noted by touching the image immediately after exposure

B: Slight tackiness was noted by touching the image immediately after exposure, but no tackiness was noted one minute after exposure

C: Tackiness was noted even one minute after exposure

<Evaluation of Substrate Adhesion Property>

On the solid image formed under different ambiances, 25 mm wide Cellotape (registered trade mark) was adhered and uniformly pressed. Thereafter, the adhered Cellotape was rapidly pulled at a peeling angle of 90 degrees and the state of the images after peeling was visually observed. The substrate adhesion property was then evaluated based on the criteria below.

[0136]

A: No image was peeled away by pulling the tape

B: Some part of the image was peeled away by pulling the tape

C: The entire contacted image was peeled away by pulling the tape

<Evaluation of Image Bleeding Resistance>

The 6-point MS Ming-cho type characters formed under different ambiences were observed employing a common magnifying glass. The state of dots adjacent to each other was observed and the image bleeding resistance was evaluated based on the criteria below.

[0137]

A: Almost no bleeding was noticed between two dots

B: Slight bleeding was noticed between two dots

C: Dots were suffered from marked bleeding

Table 1 shows the results.



[0138]

(Table 1)

| Ink No. | Printing Ambience (%RH) | Each Evaluation Result |                             |                           | Remarks             |
|---------|-------------------------|------------------------|-----------------------------|---------------------------|---------------------|
|         |                         | Ink Curability         | Substrate Adhesion Property | Image Bleeding Resistance |                     |
| 1       | 20                      | B                      | A                           | A                         | Present Invention   |
| 1       | 80                      | B                      | A                           | A                         | Present Invention   |
| 2       | 20                      | A                      | A                           | A                         | Present Invention   |
| 2       | 80                      | A                      | A                           | A                         | Present Invention   |
| 3       | 20                      | A                      | A                           | A                         | Present Invention   |
| 3       | 80                      | A                      | B                           | A                         | Present Invention   |
| 4       | 20                      | B                      | B                           | B                         | Comparative Example |
| 4       | 80                      | C                      | C                           | C                         | Comparative Example |

[0139]

(Image Evaluation B)

Image recording and evaluation were carried out in the same manner as for aforesaid Image Evaluation A, except that exposure initiating time after printing ink was varied to 0.6 second and the exposure completing time was varied to 1.1 seconds. Table 2 shows the results.

[0140]

(Table 2)

| Ink No. | Printing Ambience (%RH) | Each Evaluation Result |                             |                           | Remarks             |
|---------|-------------------------|------------------------|-----------------------------|---------------------------|---------------------|
|         |                         | Ink Curability         | Substrate Adhesion Property | Image Bleeding Resistance |                     |
| 1       | 20                      | A                      | A                           | B                         | Present Invention   |
| 1       | 80                      | B                      | B                           | B                         | Present Invention   |
| 2       | 20                      | A                      | A                           | A                         | Present Invention   |
| 2       | 80                      | A                      | A                           | B                         | Present Invention   |
| 3       | 20                      | A                      | A                           | A                         | Present Invention   |
| 3       | 80                      | A                      | A                           | B                         | Present Invention   |
| 4       | 20                      | B                      | B                           | C                         | Comparative Example |
| 4       | 80                      | C                      | C                           | C                         | Comparative Example |

[0141]

As can clearly be seen from Tables 1 and 2, inks comprising the oxetane compound of the present invention, having an electron donating group as well as an electron attractive group in the molecule, in which the 2-position is substituted, were capable of forming high quality images without bleeding which exhibited excellent ink curability as well as excellent substrate adhesion property under a high humidity ambience and various exposure ambiances, compared to

the comparative examples. Further, it is also seen that by employing the oxetane compound having no substituent at the 2-position together with the oxetane compound in which the 2-position is substituted, the resulting reactivity increased whereby the effects of the present invention were markedly enhanced.

[0142]

[EFFECTS OF THE PRESENT INVENTION]

According to the present invention, it is possible to provide oxetane compounds capable of resulting in high quality images without bleeding, which exhibit excellent ink curability as well as excellent substrate adhesion property, while not being adversely affected by ambient humidity even while employing a low illuminance light source, an ink-jet ink capable of forming high quality images, and the image forming method using the aforesaid ink-jet ink.

[NAME OF DOCUMENT]        Abstract

[SUMMARY]

[PROBLEMS TO BE SOLVED]

An object of the present invention is to provide an oxetane compound capable of forming high quality images without bleeding, which exhibits excellent ink curability and close adhesion property to substrates, being not adversely affected by ambient humidity while even employing a low illuminance light source, an ink-jet ink capable of forming high quality images, and an image forming method using the aforesaid ink-jet ink.

[MEANS TO SOLVE THE PROBLEMS]

An oxetane compound having an electron-donating group and an electron-withdrawing group in the molecule, and further having a substituent at the 2-position of the molecule.

[SELECTED DRAWINGS]        None